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Modification of the conductance of single fullerene molecules by endohedral doping

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We use scanning tunneling microscopy to establish controlled contacts to single molecules of endohedrally doped $Ce_2@C_{80}$ fullerenes with C_{60} as a reference. The stability of the experimental setup allows for the determination of the conductance of $Ce_2@C_{80}$ *relative* to the conductance of C_{60}. The endohedral doping reduces the conductance of $Ce_2@C_{80}$ by a factor of about five with respect to C_{60}. *Ab initio* calculations show that the reason for this reduced conductance is the absence of electron orbitals delocalized over the cage of $Ce_2@C_{80}$ in the energy window of the conductance measurement. © *2009 American Institute of Physics*. [doi:10.1063/1.3236529]

Measuring the electron transport properties of single molecules constitutes one of the central efforts in molecular electronics.[1] Significant contributions come from comparative studies where different molecules are introduced in a particular contact setup[2] yielding information on how the selection of the molecule determines the transport characteristic of the molecular junction. Usually, the molecular junctions are formed between close metal electrodes covered by dense populations of the molecule under investigation resulting in a stochastic character of the experiments. A statistical analysis of the results must be undertaken to select the most reproducible characteristics of the junctions.[2]

An alternative approach to characterizing nanoscale contacts showing a considerably higher degree of reproducibility has been demonstrated using low temperature scanning tunneling microscope (LT-STM). LT-STM allowed constructing atomic-size contacts between a flat substrate and a sharp tip. Its imaging capability allowed selecting desired contact geometry and modifying the contact properties by including different single atoms in the contact area.[3] Ultimately, transport properties of a single C_{60} molecule have been investigated in detail.[4–6]

Here we present a comparative LT-STM study of the conductance of molecular junctions including single endohedrally doped dimetallofullerene $Ce_2@C_{80}$ and C_{60} molecules (Fig. 1). C_{60} is an important molecular electronics model system,[6,7] and a passing reference molecule to $Ce_2@C_{80}$ since both molecules exhibit the I_h symmetry of the carbon cage. The I_h isomer of C_{80} has not been isolated so far.[8] Endohedral doping of hollow carbon cages represents a way to impose new functional properties on the fullerene-based single molecule devices due to the possibility of changing the electronic and magnetic properties of the molecules while preserving their unique highly symmetric outer shell.[9] The symmetry of metallofullerenes results in easier self-organization, and simpler bonding schemes to electrodes than observed, e.g., in molecular devices based on alkane derivatives.[10] We show that for $Ce_2@C_{80}$ the endohedral doping reduces the conductance in a single molecule junction compared to that of C_{60}. *Ab initio* calculations show that delocalized electron states of the fullerene cage mediating the conductance in C_{60} shift to higher energies in $Ce_2@C_{80}$ becoming strongly off resonance in the energy window of the conductance measurement.

Experiments were performed on a commercial ultrahigh vacuum (UHV) LT-STM operated at $T=7$ K. A Cu(111) single-crystal substrate was cleaned by repeated Ne^+ ion sputtering and annealing at 650 °C. $Ce_2@C_{80}$ was produced by the ac arc discharge method followed by isolation and purification with high-performance liquid chromatography. $Ce_2@C_{80}$ powder was degassed in UHV and evaporated from the Knudsen cell operating at 550 °C on the Cu(111) surface at room temperature. Deposition was followed by annealing to 250 °C. After annealing the sample was cooled down to $T=80$ K and exposed with thermally evaporated C_{60} molecules.

An STM image of the sample with both $Ce_2@C_{80}$ and C_{60} molecules is shown in Fig. 1(a). The molecules have been identified based on their characteristic topography images and adsorption positions obtained from reference measurements with only one type of molecule. $Ce_2@C_{80}$ appear

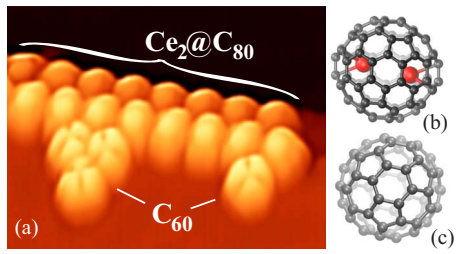

FIG. 1. (Color online) (a) STM image of sample for comparative measurement of conductance of single molecules. Image width 8 nm, $V_s=0.1$ V, $I_t=1$ nA. (b) and (c) Schematic top view of the adsorbed $Ce_2@C_{80}$ and C_{60}, respectively.

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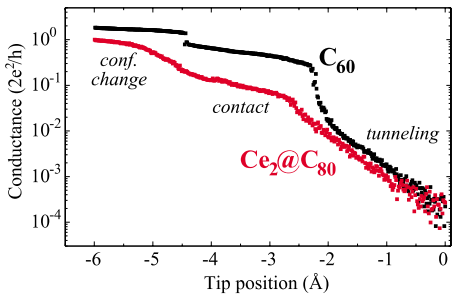

FIG. 2. (Color online) Conductance traces measured with the same STM tip on C_{60} and $Ce_2@C_{80}$ as a function of tip-molecule distance. In the contact regime the conductance of $Ce_2@C_{80}$ is ≈5 times lower than that of C_{60}.

as smooth and featureless protrusions and form ordered rows along upper and lower step edges. C_{60} adsorb at random positions, and show a clear three-lobed pattern characteristic of adsorption with an hexagonal ring pointing upwards [Fig. 1(c)].[11] Our *ab initio* calculations suggest that the preferred orientation of chemisorbed $Ce_2@C_{80}$ is similar to C_{60} [Fig. 1(b)].

The presence of both types of molecules on the surface allowed for a comparative study of their conductance to be performed in a STM junction, following Refs. 3 and 4. Before measurement, chemically etched tungsten STM tips were cleaned by *in situ* thermal annealing and stabilized by controlled indentation in the Cu substrate until a featureless spectra showing a clear onset of the Cu(111) surface state in scanning tunneling spectroscopy (STS) measurements[12] were obtained. Conductance measurements were performed by positioning the STM tip above a molecule, setting the sample voltage and the tunneling current to V_s=0.3 V and I_t =3 nA, disabling the STM feedback loop and recording the tunneling current while approaching the tip to the sample. Only measurements showing no detectable change of tip and sample both in imaging and STS after contacting the molecules were considered.

Typical conductance traces measured on C_{60} and $Ce_2@C_{80}$ are shown in Fig. 2. The conductance $G=I_t/V_s$ is expressed in units of conductance quantum $G_0=2e^2/h$ and plotted with respect to the tip displacement Δz. The trace for C_{60} shows conductance regimes that have been observed and interpreted in Ref. 4. In the tunneling regime [$\Delta z \in (0, -2.3)$ Å], the tip and the molecule are not in contact. In the contact regime [$\Delta z \in (-2.3, -4.5)$ Å], chemical bonds form between the C_{60} cage and the tip. The geometry of the C_{60} molecule remains largely unperturbed. A steplike change of I_t at Δz=−4.5 Å indicates a conformation change of the molecular junction. In spite of the conformation change, the conductance trace is perfectly reversible.

The conductance trace for $Ce_2@C_{80}$ shows the transition to contact and the conformation change as well, allowing an interpretation in terms of conductance regimes of C_{60}. The tip-cage bonds form at Δz=−2.6 Å. The conformation change is less abrupt, nevertheless taking place between $\Delta z \in (-4, -5)$ Å. In both $Ce_2@C_{80}$ and C_{60} the positions of the transition to contact vary for different measurements. However, the conductance of $Ce_2@C_{80}$ in the contact regime remains consistently ≈5 times lower than that of C_{60}. The difference in conductance is observed for all adsorption positions of the molecules in our experiment, i.e., for $Ce_2@C_{80}$ at both upper and lower step edges, and C_{60} both on terraces and at the step edges.

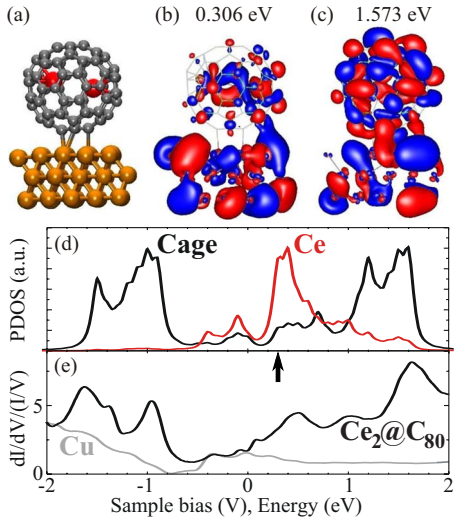

FIG. 3. (Color online) [(a)–(d)] DFT calculations of $Ce_2@C_{80}$ on Cu(111). (a) Minimum energy configuration. (b) Localized, and (c) delocalized orbitals at 0.306 and 1.573 eV above E_f. (d) Partial density of states for Ce and cage C atoms. At energy around 0.3 eV where the conductance measurements are performed [arrow in (e)] electron states localized on Ce dominate the spectrum. Electron states delocalized on the cage have energy ≥1 eV. (e) DOS measured by STS on $Ce_2@C_{80}$ and on the clean substrate.

We interpret this observation using results of *ab initio* calculations of the electron structure of C_{60} (Ref. 14) and $Ce_2@C_{80}$ (Fig. 3) adsorbed on Cu(111). Generally, calculations of molecular conductance require evaluating transmission coefficients of electron elastic scattering channels related to orbitals of the molecule-electrode system.[4,13] However, a practical conclusion has been drawn that orbitals delocalized over the whole molecule in contact show better transmission than localized ones.[13] Further, we assume that the calculated electron structure of an adsorbed metallofullerene does not change significantly after creating the tip-cage bond in the contact regime of conductance measurements as has been shown for C_{60}.[4] In free C_{60} highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are delocalized over the carbon cage and are separated by a gap of 1.7 eV at our level of theory. Upon adsorption on Cu(111) both calculations and experiment confirm splitting and shifting of the LUMO resulting in a half-filled state at E_f and an unoccupied state at ≈0.4 eV (and a state at 1.2 eV) that have both Cu and significant cage contributions (carbon content >30%) and their orbitals are delocalized over the cage.[4,14,15] The delocalized cage-Cu orbitals represent highly conductive channels for the electron transport through the C_{60} between Cu electrodes resulting in an observed conductance of about 0.5 G_0.[4]

For comparison, we perform a DFT calculation of $Ce_2@C_{80}$ on Cu(111) utilizing unconstrained geometry optimizations of $Ce_2@C_{80}$ bonded to cluster models of the Cu(111) surface. The calculations were performed with Turbomole 5.9.1 (Ref. 16) using the PBE functional and basis sets and effective core potentials (ECPs) as in previous studies of endohedrally doped fullerenes on noble metal surfaces,[17] with good quality basis set and ECP for Ce as in Ref. 18. The calculated adsorption geometry of $Ce_2@C_{80}$ on Cu(111) is shown in Fig. 3(a). We find that configurations with a six-membered ring of the C_{80}-cage bonded to the

Cu(111) surface and the cerium atoms bonded to the side walls of the cage are preferred regardless of binding site on Cu(111).

In free $Ce_2@C_{80}$ the HOMO-LUMO gap is smaller than in C_{60}, about 225 meV. Both HOMO and LUMO are localized on the encapsulated Ce atoms.[18] Upon adsorption on Cu(111), the low lying unoccupied states are dominated by Ce and Cu contributions with surprisingly low cage contributions (carbon content $<8\%$) [Fig. 3(b)]. These Ce/Cu orbitals that are localized inside the cage are strongly separated in energy from delocalized cage-Cu orbitals that are forming upon adsorption as well [Fig. 3(c)]. This separation is illustrated in Fig. 3(d) where partial density of states for Ce and cage C in the adsorbed $Ce_2@C_{80}$ is plotted. The localized Ce/Cu states dominate the unoccupied spectrum between 0 and 1 eV whereas delocalized cage-Cu orbitals have energies ≥ 1 eV. This effect can be observed in calculations of electron structure also for other $Ce_2@C_{80}$ orientations, namely C–C bond up and C1 up or C2 up.

Thus, the cage-Cu orbitals delivering high conductance in C_{60} are unavailable as conducting channels for electrons with energy up to 0.3 eV [arrow in Fig. 3(e)] used in the conductance measurement. The localization of the molecular orbitals in the available Ce/Cu states significantly reduces their conductance. In spite of a higher number of orbitals available in $Ce_2@C_{80}$ [11 Ce/Cu orbitals in the energy range (0,0.5) eV] compared to C_{60} [two cage-Cu orbitals in the same energy range] the conductance of $Ce_2@C_{80}$ is five times lower reaching 0.1 G_0. The lower conductance of $Ce_2@C_{80}$ is thus explained by the lack of conductive delocalized states in the energy range of the present conductance measurement [(0,0.5) eV]. In fact, the peak in the STS of $Ce_2@C_{80}$ in this energy range [Fig. 3(e)] originates from states that are dominated by Ce contributions with less than 8% carbon contribution.

To conclude, we performed a comparative study of the conductance of C_{60} and endohedrally doped $Ce_2@C_{80}$ in single molecule contacts created in STM. Contacts including $Ce_2@C_{80}$ show about five times lower conductance compared to those including C_{60}. Based on DFT calculations we relate this effect to the different character of the molecular states contributing to the conductance. For C_{60} these states are dominated by carbon contributions delocalized over the cage, while for $Ce_2@C_{80}$ these states are localized on the encapsulated Ce atoms.

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